Waterway Sediment Operable Unit
Harbor Island Superfund Site

TRIBUTYLTIN IN MARINE SEDIMENTS AND THE BIOACCUMULATION OF TRIBUTYLTIN: COMBINED DATA REPORT

Prepared for

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For submittal to

U.S. Environmental Protection Agency
Region 10

ESI Project No.

8/203-16.3

MAY 1999

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LIST OF ACRONYMS

AOC	Administrative Order on Consent
Battelle	Battelle Marine Sciences Laboratory
CAS	Columbia Analytical Services
COC	chain of custody
DGPS	differential global positioning system
DOC	dissolved organic carbon
ESI	EVS Solutions, Inc.
GPS	global positioning system
HDPE	high-density polyethylene
HSP	health and safety plan
Lockheed	Lockheed Martin Corporation
MSS	Marine Sampling Systems
PCB	polychlorinated biphenyl
Port	Port of Seattle
PSEP	Puget Sound Estuary Program
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
Rosa	Rosa Environmental and Geotechnical Laboratory
RPD	relative percent difference
SAP	sampling and analysis plan
SOP	standard operating procedure
SOW	statement of work
SSOU	Shipyard Sediment Operable Unit
Todd	Todd Shipyards Corporation
TOC	total organic carbon
TBT	tributyltin
USEPA	U.S. Environmental Protection Agency
WSOU	Waterway Sediment Operable Unit

1.0
INTRODUCTION

The Port of Seattle (Port), Lockheed Martin Corporation (Lockheed), and Todd Shipyards Corporation (Todd) voluntarily entered into an Administrative Order on Consent (AOC) with the U.S. Environmental Protection Agency (USEPA; May 14, 1998). The objective of the AOC and attached Statement of Work (SOW) was to evaluate risks to human health and the environment associated with the bioaccumulation of polychlorinated biphenyls (PCBs), tributyltin (TBT), and mercury at the Harbor Island Superfund Site, Waterway Sediment Operable Unit (WSOU). The SOW outlines specific tasks designed to address the importance of PCBs, TBT, and mercury concentrations within the WSOU. The WSOU is located in the West Waterway, a navigable channel of the Duwamish River on the west side of Harbor Island, and is adjacent to the Lockheed and Todd Shipyards Sediment Operable Units (SSOUs). The data and subsequent interpretation resulting from this study are expected to be useful in defining future activities regarding the SSOUs.

This report*, Tributyltin in Marine Sediments and the Bioaccumulation of Tributyltin: Combined Data Report,* fulfills Tasks 2 and 3 of the SOW. These tasks examined the ecological impacts associated with exposure to TBT within the WSOU. The two main objectives of these tasks are:

- Analyze TBT in bulk sediment and filtered and unfiltered porewater of surface sediments collected from 30 stations within the WSOU (Task 2 of the SOW)

- Conduct laboratory bioaccumulation testing for TBT using sediments selected from the same 30 stations (Task 3 of the SOW)

This report presents an assessment of the predictive relationships between concentrations of TBT in tissue and those in bulk sediment and filtered and unfiltered porewater, based on the results of the chemical analyses and bioaccumulation tests. The relationships are then used to identify areas of the West Waterway with porewater or sediment concentrations of TBT that could potentially result in tissue concentrations exceeding the TBT tissue trigger concentration. This proposed trigger concentration was established based on the results of a literature review conducted under Task 1.

Sediment was collected by EVS Solutions, Inc. (ESI); Blue Water Engineering, Seattle, WA; and Marine Sampling Systems (MSS), Burley, WA. Sediment bioaccumulation testing was conducted by Battelle Marine Science Laboratory (Battelle), Sequim, WA.

Porewater extraction and grain-size determinations were provided by Rosa Environmental & Geotechnical Laboratory (Rosa), Seattle, WA. Chemical analyses of sediment, porewater, and tissue samples were conducted by Columbia Analytical Services (CAS), Kelso, WA.

At the request of Todd Shipyards, four stations located on the Todd SSOU were added to the study (Stations TBT-31 to TBT-34). These stations and the resulting analyses and data related to them are considered for comparative purposes only; this study primarily addresses TBT contamination within the WSOU. Results from these four stations may be used for future evaluations of the adjacent SSOUs.

The rest of this document is organized as follows: Section 2.0 of this report presents the study design and methods for sample collection; porewater extraction; bioaccumulation testing; and the chemical analysis of sediment, porewater, and tissues. The results and data quality summaries for the analytical and bioaccumulation testing are presented in Section 3.0. The analysis, discussion, and trigger value comparison for TBT concentrations in tissue are presented in Section 4.0. Section 5.0 contains the references used for this report. Appendix A is the navigation report from the data collection effort. Appendices B, C, D, and E contain detailed results of sediment chemistry analyses, porewater chemistry analyses, bioaccumulation testing, and subsequent tissue chemistry analyses, respectively. Appendix F contains data validation reports, and Appendix G contains field logs. The final version of the Task 1 report, *Review of Tissue Residue Effects Data for Tributyltin, Mercury, and Polychlorinated Biphenyls*, is available as a separate document (ESI 1999a).

2.0
METHODS

To determine the concentrations of TBT (ion) in bulk sediment and the porewater of sediments from the WSOU, bulk sediment and porewater samples were withdrawn from surficial sediment samples (0 - 10 cm) which had been collected from 30 stations in the WSOU and 4 stations in the Todd SSOU (Figure 2-1 and Table 2-1). Samples of filtered and unfiltered porewater and bulk sediment were analyzed for TBT ion and ancillary parameters.

To determine the extent to which TBT in sediments from the WSOU accumulates in marine benthic species, bioaccumulation tests were conducted using 20 of the 30 samples collected from the WSOU during the field survey from which porewater samples were obtained. Twenty was determined to be an adequate number of stations to provide sufficient spatial distribution and to represent the range of porewater concentrations. The 20 samples selected were those having measured TBT concentrations in porewater greater than 0.05 μg/L TBT ion, as stipulated in the SOW (Figure 2-2). A discussion of the procedure used to select stations for bioaccumulation testing is presented in Section 2.2.3.

Bioaccumulation testing was performed by exposing *Macoma nasuta*, a suspension-feeding/filter-feeding bivalve, and *Nephtys caecoides*, a burrowing deposit-feeding polychaete, to the sediment samples for 45 days.

The bioaccumulation data, together with the sediment and porewater data, were used to evaluate the site-specific relationship between concentrations of TBT in tissue and in porewater.

2.1 STATION LOCATIONS

Stations were originally selected for this study based on historical TBT measurements and spatial coverage of the WSOU. Stations were located using a differential global positioning system (DGPS). At the start and end of each sampling day the sampling vessel was positioned at a calibration point located at the south end of the Fisher Mills dock in the West Waterway (FM-4). The GPS antenna on the sampling vessel was positioned as close to the surveyed calibration point as possible. A visual estimate of the range and bearing from the monument to the GPS antenna was made and compared to the range and bearing displayed of the screen to confirm the accuracy of the positioning system.

Figure 2-1

Table 2-1. TBT study station locations

STATION ID	LONGITUDE	LATITUDE
WSOU Stations		
TBT-001	122°21′27.00041″	47°34′27.26951″
TBT-002	122°21′34.46864″	47°34′28.74578″
TBT-003	122°21′29.43603″	47°34′30.39172″
TBT-004	122°21′31.25884″	47°34′32.21222″
TBT-005	122°21′38.54895″	47°34′31.88535″
TBT-006	122°21′39.18205″	47°34′34.37133″
TBT-007	122°21′35.07712″	47°34′34.87263″
TBT-008	122°21′31.09806″	47°34′34.99019″
TBT-009	122°21′31.10402″	47°34′38.72936″
TBT-010	122°21′38.64838″	47°34′38.70608″
TBT-011	122°21′40.13763″	47°34′42.22889″
TBT-012	122°21′30.81096″	47°34′43.86440″
TBT-013	122°21′35.82178″	47°34′44.94618″
TBT-014	122°21′39.74881″	47°34′46.77689″
TBT-015	122°21′36.33728″	47°34′48.84435″
TBT-016	122°21′31.00066″	47°34′52.18238″
TBT-017	122°21′39.09707″	47°34′53.65213″
TBT-018	122°21′31.09299″	47°34′54.48708″
TBT-019	122°21′35.58952″	47°34′58.27063″
TBT-020	122°21′38.67584″	47°34′59.33478″
TBT-021	122°21′35.06927″	47°35′00.12730″
TBT-022	122°21′32.61894″	47°35′00.35800″
TBT-023	122°21′32.45611″	47°35′02.05538″
TBT-024	122°21′33.36100″	47°35′04.79369″
TBT-025	122°21′37.12887″	47°35′04.53276″
TBT-026	122°21′31.84589″	47°35′09.60663″
TBT-027	122°21′35.14700″	47°35′10.32717″
TBT-028	122°21′35.36021″	47°35′12.84633″
TBT-029	122°21′30.77453″	47°35′14.84144″
TBT-030	122°21′35.26061″	47°35′16.59007″
Todd SSOU Stations		
TBT-031	122°21′22.84361″	47°35′15.38659″
TBT-032	122°21′22.09038″	47°35′20.75216″
TBT-033	122°21′17.80420″	47°35′18.60318″
TBT-034	122°21′30.12346″	47°35′03.23608″

NOTE: Survey datum = NAD83

Figure 2-2

The actual station locations sampled and positions recorded are presented in Figure 2-1 and Table 2-1. Locations are accurate to within ± 1 m. The complete navigation report in contained in Appendix A.

2.2 SEDIMENT SAMPLES

Sediment collection field activities took place from Wednesday, July 15 through Friday, July 17, 1998. The R/V *Nancy Anne*, provided by MSS, served as the sampling platform. There were no substantial deviations from the sampling and analysis plan (SAP; EVS 1998).

2.2.1 Field Methods

Surface sediment samples (0-10 cm) were collected from 30 stations in the WSOU and 4 stations in the Todd SSOU using a modified, hydraulic-assisted, stainless-steel van Veen grab sampler. Sediment was removed from the sampler using stainless steel spoons and placed into a 10-gallon high-density polyethylene (HDPE) bucket for homogenization. Successive grabs were taken until a sufficient quantity of sediment for all analyses was obtained. The sediment was then homogenized using a handheld power drill with a stainless steel mixing paddle. Aliquots of sediment were then transferred to the appropriate sample containers. Sediment collected for porewater extraction and bioaccumulation analysis was stored under anaerobic conditions, maintained by flooding the headspace of the sample containers with nitrogen. More detailed information on the methodology used for sample collection can be found in Section 3.4.2 of the SAP (EVS 1998).

Three types of field quality assurance samples were collected during surface sediment sampling as specified in the quality assurance project plan (QAPP; EVS 1998): four field homogenate replicates, two cross contamination blanks of the compositing equipment, and a filter blank. Field homogenate replicates were collected at Stations TBT-02, TBT-07, TBT-14, and TBT-28 and were submitted blind, as separate samples, to the laboratories for analysis.

2.2.2 Chemical Analyses

Bulk sediment samples were analyzed by CAS for TBT (reported as μg/kg ion) and total organic carbon (TOC). Grain-size analyses were conducted by Rosa. Methods, holding times, target detection limits, method detection limits, and quality assurance/quality control (QA/QC) samples are discussed in Section 7.0 of the QAPP (EVS 1998). A laboratory audit conducted by Bruce Woods of USEPA on July 22, 1998, indicated that there were no significant deviations in the laboratory's procedures that adversely affected the data quality. Detailed results of chemical analyses of bulk sediment are provided in Appendix B.

2.2.3 Bioaccumulation Testing

The selection of sediments for bioaccumulation testing was based on the sediment and porewater concentrations of TBT. The concentrations were ranked from lowest to highest for sediment, filtered porewater, and unfiltered porewater (Table 2-2). Three stations that had porewater concentrations below 0.05 µg/L TBT (TBT-01, TBT-10, and TBT-17) and the four stations that were sampled from the Todd SSOU were not considered for bioaccumulation testing. Station TBT-29 was not selected for testing because the measured TBT concentrations appeared to be outliers when compared to the complete dataset. The final selection of the stations for testing provided a representative range of TBT concentrations and a geographical distribution throughout the WSOU. Sediments recommended for testing were presented to USEPA for approval in a meeting on August 19, 1998. The stations selected and subsequently tested for bioaccumulation are presented in Figure 2-2. Results of the chemical analyses of porewater are summarized in Section 3.2 of this report and presented in Appendix C.

Bioaccumulation testing was performed by Battelle with 20 of the 30 samples collected in the WSOU using *M. nasuta* and *N. caecoides*. The two species were tested together in the same aquaria. To avoid having to extrapolate standard 28-day bioaccumulation testing results to theoretical steady-state conditions, the test was extended to a maximum of 45 days to provide a better experimental estimate of steady-state tissue concentrations (EVS 1996). Sediment additions were performed in accordance with discussions with USEPA (Boese 1998) and USEPA guidance (USEPA 1993).

Only one replicate was tested for 17 of the 20 test sediments. For the remaining three test sediments, five replicate aquaria were used to provide a measure of potential variations in tissue concentrations associated with West Waterway sediments. The replicated test sediments were selected from four randomly determined stations from which extra sediment was collected during the field survey.

The bioaccumulation data are being used to delineate areas of the West Waterway which have porewater TBT concentrations high enough to result in tissue TBT concentrations that may exceed the trigger value established as part of Task 1 of the SOW. The bioaccumulation tests for all 20 samples were not replicated, because single measurements of tissue concentration are sufficient for the purpose of establishing areas that exceed the trigger concentration.

Table 2-2. Rankings by TBT concentration of stations selected for bioaccumulation testing

STATION	BULK SEDIMENT[a] TBT (μg/kg)	STATION	FILTERED POREWATER[b] TBT (μg/L)	STATION	UNFILTERED POREWATER[b] TBT (μg/L)
TBT-10	8	TBT-10	0.01	TBT-10	0.01
TBT-01	31	TBT-01	0.02	TBT-17	0.02
TBT-11	130	TBT-17	0.02	TBT-01	0.06
TBT-18	210	TBT-18	0.06	TBT-18	0.08
TBT-25	310	TBT-19	0.06	TBT-19	0.08
TBT-30	310	TBT-11	0.07	TBT-11	0.1
TBT-04	330	TBT-22	0.09	TBT-26	0.17
TBT-22	350	TBT-06	0.11	TBT-07[c]	0.21
TBT-08	400	TBT-15	0.13	TBT-05	0.22
TBT-19	450	TBT-26	0.13	TBT-15	0.24
TBT-23	510	TBT-23	0.14	TBT-23	0.24
TBT-15	530	TBT-24	0.14	TBT-09	0.27
TBT-03	540	TBT-04	0.15	TBT-04	0.29
TBT-17	560	TBT-05	0.16	TBT-22	0.29
TBT-24	570	TBT-07[c]	0.16	TBT-06	0.3
TBT-21	610	TBT-08	0.21	TBT-24	0.33
TBT-06	660	TBT-09	0.21	TBT-16	0.36
TBT-28[c]	670	TBT-12	0.24	TBT-02[c]	0.38
TBT-05	680	TBT-25	0.26	TBT-08	0.38
TBT-02[c]	690	TBT-02[c]	0.265	TBT-25	0.44
TBT-27	730	TBT-13	0.37	TBT-13	0.47
TBT-09	800	TBT-21	0.38	TBT-03	0.51
TBT-07[c]	820	TBT-20	0.41	TBT-12	0.51
TBT-12	830	TBT-16	0.44	TBT-21	0.51
TBT-14[c]	1050	TBT-14[c]	0.445	TBT-28[c]	0.69
TBT-13	1100	TBT-03	0.45	TBT-14[c]	0.715
TBT-26	1100	TBT-28[c]	0.575	TBT-30	0.9
TBT-16	1200	TBT-27	0.71	TBT-27	0.97
TBT-20	3500	TBT-30	0.76	TBT-20	1.01
TBT-29	6200	TBT-29	1.29	TBT-29	1.87

NOTE: Shaded area represents stations selected for bioaccumulation testing

[a] Complete data results for sediment are presented in Table 3-1.
[b] Complete data results for filtered and unfiltered porewater are presented in Table 3-2.
[c] Mean of two replicates.

Bioaccumulation tests followed standard QA/QC procedures, including the use of negative controls, positive controls, replicates (for three test sediments), and water quality measurements as described in Section 8.0 of the QAPP (EVS 1998). The QA/QC data and the results of the QA/QC procedures are summarized in Section 3.3.1 and presented in Appendix D of this report.

2.3 POREWATER SAMPLES

2.3.1 Extraction Methods

Two gallons of sediment from each of the 34 locations was sent to Rosa for porewater extraction. Sediment samples were transported in HDPE buckets with nitrogen-purged headspace. The porewater extraction was performed under anaerobic conditions in a nitrogen atmosphere. Sediment samples were double-centrifuged at 4°C: first at 3,000 rpm (2,700 G) for 30 min; the resulting supernatant was removed and centrifuged again at 9,000 rpm (14,300 G) for 30 min.[1] One half (approximately 500 mL) of the supernatant from the second centrifugation was then filtered through a 0.45-μm silver filter. The filtered and unfiltered porewater samples were acidified with HCl for preservation until analysis of TBT. A separate extraction was performed for the unfiltered dissolved organic carbon (DOC) and filtered DOC analyses. The porewater samples were then shipped to CAS for TBT and organic carbon analysis. The Rosa case narrative with details of the extraction methodology is presented in Appendix C.

2.3.2 TBT Analysis

CAS performed all chemical analyses conducted on the porewater samples. Methods, holding times, target detection limits, method detection limits, and QA/QC controls are discussed in Section 7.0 of the QAPP and in Appendix D of the SAP (EVS 1998). The results of the porewater analyses are discussed in Section 3.2 and Appendix C of this report.

2.4 TISSUE SAMPLES

At the completion of the 45-day bioaccumulation testing and 24-hr depuration period in clean flowing seawater, tissue samples were collected from *M. nasuta* and *N. caecoides*. A total of 37 samples was collected for each species, including 17 samples from the single replicate treatments, 15 samples from the three treatments with five replicates, and 5 replicate samples from the control treatments. Because of reduced survival and

1. The laboratory inadvertently centrifuged the sample at 9,000 rpm rather the 9,000 g specified in the QAPP. It is uncertain what effect, if any, this may have had on the resulting supernatant.

consequent low tissue volumes for the *N. caecoides* samples, tissues from the surviving organisms in the control replicates were composited and split into five replicates for analysis at CAS. All tissue samples were frozen immediately and stored at temperatures below -20°C. Samples were shipped by overnight courier to CAS for analysis of TBT and percent lipids.

CAS performed all chemical analyses on tissue samples. The data are considered usable as qualified. Methods, holding times, target detection limits, method detection limits, and QA/QC controls are discussed in Section 7.0 of the QAPP (EVS 1998). The results of the tissue analyses are discussed in Section 3.4 and Appendix E of this report.

2.5 DATA EVALUATION

Exploratory data analysis was used to determine evidence of linear relationships between sediment, porewater, and tissue TBT concentrations. Linear regressions were applied to pairs of variables that had evidence of a linear relationship in linear or log (base 10) units. The relative strengths of these relationships were described by the magnitude of R^2. All statistical analyses were conducted using S-PLUS™ statistical software (version 4.5, MathSoft, Inc.).

3.0
RESULTS

3.1 SEDIMENT SAMPLES

3.1.1 Data Summary

The bulk sediment TBT concentrations (as TBT ion) ranged from a minimum of 8 μg/kg dry weight at Station TBT-10 to a maximum of 6,600 μg/kg dry weight at Station TBT-31 (Table 3-1). The concentrations of TBT in sediment ranged over 3 orders of magnitude. When the two lowest and two highest concentrations are excluded, the range from lowest to highest is only 30-fold. The variability of TBT concentrations measured among field homogenization replicates ranged from 6 to 31 percent for the four replicates tested. With the exception of Station TBT-01, there was a general trend of decreasing TOC and fractions of fine-grained material approaching the mouth of the waterway. Sediments collected adjacent to Harbor Island tended to be richer in organic material and finer than sediments collected from middle channel or east side stations. Overall, the TBT and organic carbon concentrations and grain-size characteristics were consistent with the sediments collected from previous studies in the West Waterway (EVS and Hart Crowser 1995).

Concentrations of TOC in bulk sediment (percent of dry weight) ranged from a minimum of 0.5 percent for Station TBT-10 to a maximum of 4.24 percent at Station TBT-34. Sediment grain-size analysis showed a minimum of 10.16 percent fines at Station TBT-01 and a maximum of 77.19 percent fines at Station TBT-12. As expected, sediment TOC correlated positively with percent fines. The sediment sample from Station TBT-34 was an exception to this correlation, having a high concentration of organic carbon and a low fraction of fine-grained material.

3.1.2 Data Quality

All analyses were performed in a manner consistent with the methods and guidelines stated in the QAPP. No substantial deviations from the QAPP occurred. All recommended holding times were met for the sediment sample analyses. The results of all laboratory analyses including the case narrative, test sediments, and QA/QC samples are presented in Appendix B. The chemistry data were independently reviewed and validated by Quality by Design. The data are considered usable as reported and qualified. The complete data validation report is presented in Appendix F.

Table 3-1. Sediment chemistry and conventional parameters

Station	TBT Ion (μg/kg)	Total Organic Carbon (%)	Total Solids (%)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Fines (%)
TBT-01	31	0.58	74.3	11.8	78.0	6.48	3.68	10.2
TBT-02	730	2.09	54.8	0.17	33.6	45.7	20.6	66.3
TBT-03	540	2.01	53.5	5.40	30.9	39.8	23.9	63.7
TBT-04	330	1.10	64.2	1.11	58.4	25.3	15.2	40.5
TBT-05	680	1.83	52.6	0.00	32.6	44.0	23.4	67.4
TBT-06	660	1.81	53.9	0.05	35.2	41.2	23.6	64.8
TBT-07	670	1.66	52.8	0.16	38.2	42.1	19.6	61.7
TBT-08	400	3.25	48.4	4.17	39.9	35.4	20.5	56.0
TBT-09	800	2.02	49.6	1.43	27.2	46.6	24.8	71.4
TBT-10	8	0.50	72.5	0.73	75.9	18.2	5.18	23.4
TBT-11	130	0.75	67.0	0.73	70.0	22.0	7.19	29.2
TBT-12	830	2.30	51.7	2.47	20.3	49.1	28.1	77.2
TBT-13	1,100	1.31	59.1	2.11	52.3	29.4	16.2	45.6
TBT-14	1,100	1.03	60.4	8.72	52.5	25.2	13.6	38.8
TBT-15	530	1.35	63.2	5.39	56.0	26.4	12.2	38.6
TBT-16	1,200	2.07	52.7	0.70	37.9	37.2	24.2	61.4
TBT-17	560	0.86	66.6	0.06	71.4	22.2	6.37	28.5
TBT-18	210	1.15	77.7	0.66	70.8	18.3	10.2	28.6
TBT-19	450	1.22	60.5	2.34	44.4	37.7	15.5	53.2
TBT-20	3,500	1.60	56.5	3.44	44.5	33.3	18.8	52.1
TBT-21	610	1.23	61.1	1.17	52.2	33.9	12.8	46.6
TBT-22	350	0.94	64.8	0.13	61.5	27.8	10.5	38.3
TBT-23	510	0.93	65.5	0.03	61.6	27.7	10.6	38.3
TBT-24	570	1.27	60.0	0.13	50.9	34.6	14.4	49.0
TBT-25	310	1.12	63.6	0.85	44.7	42.4	12.0	54.4
TBT-26	1,100	1.21	60.0	1.14	70.6	19.0	9.25	28.3
TBT-27	730	1.45	63.4	10.5	54.1	24.6	10.8	35.5
TBT-28	690	1.22	60.0	0.08	52.0	35.5	12.4	47.9
TBT-29	6,200	2.41	46.3	1.21	53.5	30.7	14.6	45.3
TBT-30	310	1.28	61.2	1.17	42.6	42.1	14.2	56.3
TBT-31	6,600	1.70	51.0	5.09	58.7	25.2	11.1	36.3
TBT-32	2,200	0.99	61.8	0.33	67.6	22.0	10.1	32.1
TBT-33	1,000	1.25	61.1	0.59	80.9	12.8	5.70	18.5
TBT-34	850	4.24	51.6	27.3	42.8	18.7	11.2	29.9
TBT-35[a]	650	1.89	55.6	0.00	33.2	44.9	22.0	66.8
TBT-36[b]	970	1.71	54.1	0.53	40.2	39.6	19.6	59.3
TBT-37[c]	1,000	1.22	63.2	9.68	51.1	25.9	13.3	39.2
TBT-38[d]	650	1.40	61.3	0.48	51.4	36.0	12.1	48.2

[a] Homogenate replicate collected at station TBT-02.
[b] Homogenate replicate collected at station TBT-07.
[c] Homogenate replicate collected at station TBT-14.
[d] Homogenate replicate collected at station TBT-28.

3.2 POREWATER SAMPLES

3.2.1 Data Summary

TBT concentrations (as TBT ion) in unfiltered porewater ranged from a minimum of 0.01 μg/L at Station TBT-10 to a maximum of 1.87 μg/L at Station TBT-31 (Table 3-2). TBT concentrations (as TBT ion) in filtered porewater ranged from a minimum of 0.01 μg/L at Station TBT-10 to a maximum of 1.49 μg/L at Station TBT-31.

DOC concentrations in unfiltered porewater ranged from a minimum of 7.8 mg/L at Station TBT-10 to a maximum of 39.9 mg/L at Station TBT-25. DOC concentrations in filtered porewater ranged from a minimum of 6.3 mg/L at Station TBT-33 to a maximum of 32.9 mg/L at Station TBT-25 (Table 3-2).

The effect of filtering the samples can be evaluated by comparing the TBT concentrations in unfiltered and filtered porewater, as well as the differences between unfiltered DOC and filtered DOC concentrations. In general, the filtered samples had lower TBT concentrations than the unfiltered samples, although one sample had a filtered concentration that was 22 percent higher than the unfiltered concentration. The greatest loss of TBT was 69 percent of the unfiltered concentration. The mean change in concentration over all porewater samples was a loss of 30 percent of the initial or unfiltered TBT concentration. A similar difference was seen between the unfiltered DOC and filtered DOC concentrations. In general, the filtered DOC concentrations were less than the corresponding unfiltered DOC concentrations, although one sample, TBT-27, had a DOC concentration that was 107 percent higher than the unfiltered DOC concentration. The greatest loss was 42 percent of the unfiltered DOC concentration. The mean difference over all porewater samples was a loss of 7 percent of the unfiltered DOC concentration. If sample TBT-27 is excluded from the mean, the mean was a loss of 10 percent of the unfiltered DOC concentration.

There was no consistent relationship between the concentration of TBT in unfiltered and filtered samples and the difference between the unfiltered DOC and filtered DOC concentrations. The samples with the greatest loss of TBT did not correspond to the samples with the greatest difference between their unfiltered DOC and filtered DOC concentrations. Most of the differences were within the range of analytical uncertainty.

The homogenate replicate relative percent differences (RPDs) for TBT and DOC measured in filtered porewater ranged from 23 to 87 percent and 12 to 73 percent, respectively. The homogenate replicate RPDs for TBT and DOC measured in unfiltered porewater ranged from 14 to 53 percent and 2 to 78 percent, respectively.

Table 3-2. Filtered and unfiltered porewater chemistry

Station	TBT-Filtered (μg/L)	Filtered Dissolved Organic Carbon (mg/L)	TBT-Unfiltered (μg/L)	Unfiltered Dissolved Organic Carbon (mg/L)
TBT-01	0.02	10.2	0.06	13.8
TBT-02	0.38	8.7	0.48	10.5
TBT-03	0.45	19.7	0.51	24.7
TBT-04	0.15	17.2	0.29	19.6
TBT-05	0.16	12.9	0.22	14.8
TBT-06	0.11	14.0	0.30	15.9
TBT-07	0.13	12.5	0.16	11.0
TBT-08	0.21	14.3	0.38	15.2
TBT-09	0.21	12.7	0.27	12.6
TBT-10	0.01	7.6	0.01	7.8
TBT-11	0.07	12.2	0.10	21.2
TBT-12	0.24	17.4	0.51	18.9
TBT-12R[a]	0.37	nr	0.46	nr
TBT-13	0.37	7.4	0.47	8.8
TBT-14	0.31	16.3	0.58	16.9
TBT-15	0.13	11.4	0.24	13.3
TBT-16	0.44	15.3	0.36	15.0
TBT-17	0.02	8.9	0.02	8.4
TBT-18	0.06	14.6	0.08	15.4
TBT-19	0.06	7.7	0.08	8.5
TBT-20	0.41	14.3	1.01	16.6
TBT-21	0.38	13.8	0.51	15.7
TBT-22	0.09	24.7	0.29	32.7
TBT-23	0.14	14.1	0.24	14.6
TBT-24	0.14	17.0	0.33	18.7
TBT-25	0.26	32.9	0.44	39.9
TBT-26	0.13	13.1	0.17	13.3
TBT-27	0.71	29.6	0.97	14.3
TBT-28	0.64	17.4	0.74	18.5
TBT-29	1.29	9.4	1.87	10.7
TBT-30	0.76	30.0	0.90	22.4
TBT-31	1.49	14.5	1.50	15.1
TBT-32	0.28	16.4	0.35	18.7
TBT-33	0.09	6.3	0.11	8.0
TBT-34	0.14	14.4	0.19	18.6
TBT-35[b]	0.15	18.6	0.28	24.0
TBT-36[c]	0.19	11.1	0.26	11.2
TBT-37[d]	0.58	19.8	0.85	24.3
TBT-38[e]	0.51	22.4	0.64	28.0

NOTE: nr - not reported

[a] Reanalyzed sample.

[b] Homogenate replicate collected at station TBT-02.

[c] Homogenate replicate collected at station TBT-07.

[d] Homogenate replicate collected at station TBT-14.

[e] Homogenate replicate collected at station TBT-28.

The difference in measurements between the replicates can be attributed to analytical variability, matrix complexity, and sediment heterogeneity.

3.2.2 Data Quality

All analyses were performed in a manner consistent with the methods and guidelines of the QAPP with the following exceptions:

- The recommended holding time of 7 days, which included collection, extraction, and analysis, was met for 64 of the 76 porewater samples. However, the filtered and unfiltered porewater samples from Stations TBT-15, TBT-16, TBT-17, TBT-18, TBT-19, and TBT-20, were mishandled at the analytical laboratory and had to be re-extracted from the bulk sediment and re-analyzed. The re-extraction was performed 12 days after the samples were collected. An additional sample from Station TBT-12 was also re-extracted and re-analyzed to provide a basis for comparing samples that met their holding times with samples that did not. The results from the second analysis of TBT-12 were within 35 percent and 11 percent of the initial results for filtered and unfiltered porewater, respectively. These measurements are within the data quality objectives for precision of $\pm$ 40 percent as outlined in the QAPP (EVS 1998). Therefore, all data are considered usable as reported and qualified.

- The laboratory inadvertently performed the centrifugation at speeds in rpms rather than in Gs. This resulted in the second centrifugation being performed at the higher rate of 14,300 G (9,000 rpm) rather than the recommended 9,000 G.

The results of all laboratory analyses, including the case narrative and results for porewater and QA/QC samples, are presented in Appendix C. The chemistry data were independently reviewed and validated by Quality by Design. The complete data validation report is presented in Appendix F.

3.3 BIOACCUMULATION TESTING

Survival in the native control sediments was 95 percent for *M. nasuta* and 66 percent for *N. caecoides*. If an outlier *N. caecoides* replicate which had 33 percent survival is removed, mean survival in control sediments was 74 percent for *N. caecoides*. Both a low TOC content of 0.07 percent in the control sediment and the extended exposure period may have been contributing factors to reduced survival.[2] Survival of *M. nasuta* in test sediments ranged from 93.3 percent to 100 percent, with a mean survival of 97.1 percent. Survival of *N. caecoides* in test sediments ranged from 64.4 percent to 95.6 percent, with a mean survival of 83.96 percent. The relative good health of *N. caecoides* in the test treatments suggests that this organism's poor survival in control sediment was not the result of a weak strain of test organism or due solely to the duration of the test.

All water quality parameters were within acceptable ranges throughout the test. The water-only reference toxicant tests using copper resulted in an LC50 of 2.05 mg/L Cu for *M. nasuta,* which is within the laboratory acceptable range of 0.28 mg/L - 2.8 mg/L Cu; and an LC50 of 0.10 mg/L Cu for *N. caecoides,* which is within literature reported values 0.09 mg/L to 0.16 mg/L Cu (Appendix D). Based on the results of the organism survival, reference toxicant tests, and water quality observations, the bioaccumulation tests are considered acceptable. Table 3-3 presents the survival data for *M. nasuta* and *N. caecoides*. The complete case narrative for the bioaccumulation tests, including water quality observations and reference toxicant results, is found in Appendix D.

2. The supplier of *N. caecoides* (John Brezina and Associates, Dillon Beach, CA) collects the organisms and the control sediment from two nearby, but slightly different sites. The organisms are collected from an area of high population density and high amount of organic debris. In previous studies at several laboratories the organic debris has interfered with the use of the sediment at this site as a negative control, because of the effects of organic debris decaying during sediment holding. Therefore, control sediments have intentionally been collected from a nearby site with less organic debris, where *N. caecoides* is present at lower population densities. It is possible that the TOC content of the control sediment collected for this study was too low to support the required number of organisms for the extended duration (45 days) of the test, despite periodic sediment replenishment (Gardiner pers. comm. 1999b).

Table 3-3. Summary of survival of *M. nasuta* and *N. caecoides* in 45-day bioaccumulation tests

	N. caecoides		*M. nasuta*	
Treatment	Mean Percent Survival	Standard Deviation	Mean Percent Survival	Standard Deviation
Native Control	65.8	25.1	95.3	4.5
TBT-02	95.6	na	100.0	na
TBT-04	88.9	na	96.7	na
TBT-05	88.9	na	96.7	na
TBT-07	88.9	na	96.7	na
TBT-08	68.9	na	100.0	na
TBT-09	86.7	na	100.0	na
TBT-11	82.2	na	100.0	na
TBT-12	88.9	na	93.3	na
TBT-13	87.1	7.4	93.3	7.8
TBT-14	88.9	na	96.7	na
TBT-15	64.4	na	96.7	na
TBT-18	88.9	na	96.7	na
TBT-19	87.6	8.0	98.0	3.0
TBT-20	68.9	na	96.7	na
TBT-21	77.8	na	93.3	na
TBT-22	64.4	na	93.3	na
TBT-24	91.1	na	100.0	na
TBT-26	91.1	na	100.0	na
TBT-28	91.1	na	96.7	na
TBT-30	88.9	4.2	96.7	5.8

NOTE: na - not applicable; one replicate

3.4 TISSUE SAMPLES

3.4.1 Data Summary

TBT concentrations in *M. nasuta* ranged from a minimum of 4 µg/kg wet weight at Station TBT-08 to a maximum of 380 µg/kg wet weight at Station TBT-20 (Table 3-4). The percent lipids in *M. nasuta* ranged from a minimum of 2.86 percent dry weight at Station TBT-07 to a maximum of 5.26 percent dry weight at Station TBT-28.

Table 3-4. Tissue chemistry for *M. nasuta* and *N. caecoides*

	M. nasuta			*N. caecoides*		
Station	TBT (µg/kg wet wt)	Lipids (% dry wt)	Total Solids (%)	TBT (µg/kg wet wt)	Lipids (% dry wt)	Total Solids (%)
TBT-00[a]	2.0 U	4.66	16.6	2.0 U	6.23	19.9
TBT-02	21	4.05	16.3	118	6.07	11.7
TBT-04	99	4.30	15.8	92	6.71	15.8
TBT-05	15	4.76	14.7	117	7.78	18.0
TBT-07	52	2.86	15.4	129	8.82	14.4
TBT-08	4.0	4.53	15.0	15	6.59	17.0
TBT-09	18	4.31	16.0	114	5.35	21.3
TBT-11	13	4.23	15.6	101	5.78	18.5
TBT-12	25	4.83	14.7	134	6.97	16.5
TBT-13[a]	177	4.02	15.2	211	5.79	19.1
TBT-14	94	4.88	16.6	192	5.96	17.8
TBT-15	9.0	3.67	15.0	131	4.94	17.2
TBT-18	25	3.46	15.9	90	5.82	17.7
TBT-19[a]	30	5.22	15.2	68	5.51	16.3
TBT-20	376	4.15	14.7	384	5.70	16.5
TBT-21	14	4.11	15.1	120	7.43	14.4
TBT-22	10	3.95	15.2	89	6.80	16.9
TBT-24	11	4.81	15.8	104	5.96	19.3
TBT-26	195	4.39	15.5	359	5.30	16.4
TBT-28	43	5.26	15.4	130	8.00	14.5
TBT-30[a]	47	4.13	15.1	66	8.95	15.9

NOTE: U - not detected at detection limit shown

[a] Mean of five replicates.

TBT concentrations in *N. caecoides* ranged from a minimum of 15 µg/kg wet weight at Station TBT-08 to a maximum of 380 µg/kg wet weight at Station TBT-20. The percent lipids in *N. caecoides* ranged from a minimum of 4.94 percent dry weight at Station TBT-15 to a maximum of 8.95 percent dry weight at Station TBT-30.

The relationships among porewater, sediment, and tissue TBT concentrations are analyzed and discussed in Section 4.3.

The mean, standard deviation, and coefficient of variation (standard deviation/mean) of TBT concentrations for the bioaccumulation replicates are presented in Table 3-5.

Table 3-5. Tributyltin concentrations for replicated bioaccumulation tests

	STATION		
	TBT-13	TBT-19	TBT-30
M. nasuta			
Mean (µg/kg wet wt)	177	29.8	47.4
Standard deviation (µg/kg wet wt)	102	21.8	36.9
Coefficient of variation	57.7%	73.2%	77.9%
N. caecoides			
Mean (µg/kg wet wt)	211	67.8	65.6
Standard deviation (µg/kg wet wt)	17.4	7.16	10.1
Coefficient of variation	8.3%	10.6%	15.3%

This table clearly shows that results for *M. nasuta* were more variable than results for *N. caecoides*. The difference in variability between the tissue values in *M. nasuta* and *N. caecoides* is possibly due to the inherent variability of feeding regimes of the two species. *N. caecoides* is a mobile sediment deposit feeder whose feeding activities result in a greater integration of sediment within the aquaria. *M. nasuta* is a more stationary organism that feeds on surface sediments and filters overlying water. Greater variability in *M. nasuta* tissue concentrations may be due to the fact that feeding is limited to sediment in the organism's immediate vicinity. Any heterogeneity in sediment TBT concentrations within or between the aquaria might be reflected in the *M. nasuta* tissue concentrations. The coefficients of variation are highly consistent across replicates for intraspecies comparisons.

From a statistical standpoint, the fit of a regression line can be evaluated using R^2 values defined as the percent of total variability in tissue concentrations "explained" by the regression model. The residual, or "unexplained" variance can be broken down into pure error, or the intrinsic variability among replicates as shown in Table 3-5, plus the lack-of-fit error associated with deviations from the linear model. While the absolute magnitude of the replicate variability for *M. nasuta* is larger than that for *N. caecoides*, what is relevant is whether the ratio of replicate variability to residual variance is greater for one species than for the other. For a fixed R^2 value, if the replicate variability for one species makes up a greater proportion of the residual variance, this suggests a better linear fit because it means that the lack-of-fit error makes up a smaller proportion of the residual variance. However, neither of the regression models is subsequently used, because of poor overall fit; whether the source of this poor fit is intrinsic variability in the test or a poor linear fit is irrelevant.

3.4.2 Data Quality

All analyses were performed consistent with the methods and guidelines as stated in the QAPP. All recommended holding times were met for the tissue sample analyses. Because of an error in initial extraction of the sample for the lipid analysis, CAS re-extracted and analyzed the samples for lipids using the method in Bligh and Dyer (1959) referenced in the QAPP. The re-analysis occurred within the recommended holding time of 1 year. For the *N. caecoides* control samples, the sample quantity available limited re-analysis to one sample replicate. Since the replicate sample was created from a composite, the lipid result should be considered representative of each of the replicates originally tested. The data are considered usable as reported and qualified. The results of all laboratory analyses, including the case narrative, test tissues, and QA/QC samples, are presented in Appendix E. The chemistry data were independently reviewed and validated by Quality by Design. The complete data validation report is presented in Appendix F.

At the completion of the test, lipid contents were within the range expected for healthy organisms based on the mean values from previous studies—*M. nasuta* 1.4 to 6.3 percent; polychaetes 5.0 to 16.7 percent; no specific data for *N. caecoides* (Gardiner pers. comm. 1999a). The range for *M. nasuta* was 2.86 to 5.26 percent dry weight and the range for *N. caecoides* was 4.94 to 8.95 percent dry weight.

4.0
DISCUSSION

The bioavailability of sediment contaminants has been shown to be affected both by the chemical and environmental speciation of the contaminant, and by the behavior and physiology of the organisms. The two primary routes of exposure for organisms in sediments are transport of dissolved contaminants in sediment porewater across biological membranes and the ingestion of contaminated sediment particles. Exposure to dissolved contaminant concentrations in sediment porewaters appears to be the predominant route of exposure for many benthic organisms (Muir et al. 1985; Oliver 1987; Shaw and Connell 1987). However, exposure from sediment ingestion may be an important route of exposure for some species (Landrum 1989; Harkey et al. 1994; Meador et al. 1995).

TBT in marine sediments can exist in a variety of different forms, including TBT sorbed to sediment particles, and, in sediment porewaters, free ions, inorganic TBT complexes, and TBT associated with organic colloids. TBT has a relatively high affinity for organic carbon, reflected in the measured octanol-water partition coefficient (log K_{ow}) for this compound of 4.41 (Arnold et al. 1998). Several studies have shown that the distribution of TBT between sediment particles and porewater can be related to the organic carbon content of the sediment (Harris and Cleary 1987; Meador et al.1997). TBT sorption has also been related to the clay content of sediments (Dooley and Homer 1983). Several authors have suggested that the presence of TBT associated with paint chips in the sediment can influence the bioavailability of the compound in the field (Parametrix 1995; Weston 1996).

During this study, the second centrifugation of the porewater samples that was conducted for 30 minutes at 9,000 rpm removed suspended particulate material and a substantial fraction of the large colloidal material. The remaining samples were then analyzed directly or filtered through a 0.45 micron filter and analyzed. Both the filtered and unfiltered porewater samples contained dissolved TBT and possibly TBT associated with colloidal organic macromolecules that were not removed during the centrifugation of the sample.

The TBT concentrations measured in *N. caecoides* are compared with the bulk sediment and porewater concentrations measured for the same samples used in the bioaccumulation testing in Table 4-1 and Figure 4-1.

Table 4-1. TBT concentrations in *N. caecoides*, sediment, and porewater

	N. caecoides (μg/kg)			Sediment (μg/kg)		Porewater (μg/L)	
Rank[a]	Wet Weight	Dry Weight	Station	Bulk	TOC-normalized	Filtered	Unfiltered
1	15.0	88.0	TBT-08	400	12,300	0.21	0.38
2	65.6[b]	417	TBT-30	310	24,200	0.76	0.90
3	67.8[b]	416	TBT-19	450	36,900	0.06	0.08
4	89.0	527	TBT-22	350	37,200	0.09	0.29
5	90.0	508	TBT-18	210	18,300	0.06	0.08
6	92.0	582	TBT-04	330	30,000	0.15	0.29
7	101	546	TBT-11	130	17,300	0.07	0.10
8	104	539	TBT-24	570	44,900	0.14	0.33
9	114	535	TBT-09	800	39,600	0.21	0.27
10	117	650	TBT-05	680	37,200	0.16	0.22
11	118	1,010	TBT-02[c]	690	34,700	0.27	0.38
12	120	833	TBT-21	610	49,600	0.38	0.51
13	129	896	TBT-07[c]	820	48,700	0.16	0.21
14	130	897	TBT-28[c]	670	51,100	0.57	0.69
15	131	762	TBT-15	530	39,300	0.13	0.24
16	134	812	TBT-12	830	36,100	0.30	0.48
17	192	1,080	TBT-14[c]	1,050	93,300	0.45	0.71
18	211[b]	1,140	TBT-13	1,100	84,000	0.37	0.47
19	359	2,190	TBT-26	1,100	90,900	0.13	0.17
20	384	2,330	TBT-20	3,500	219,000	0.41	1.01

[a] Rank order determined by TBT concentration in *N. caecoides* (wet weight).
[b] Average of 5 replicate bioassays.
[c] Sediment concentrations at these stations are means of two homogenate replicates (see Table 3-1).

Figure 4-1

The relationship between the *N. caecoides* tissue concentrations and the organic carbon-normalized sediment concentrations appears to be stronger than the relationship with the filtered and unfiltered porewater concentrations. These relationships will be explored in more detail in the following sections.

The TBT concentrations measured in *M. nasuta* are compared with the sediment and porewater TBT concentrations in Table 4-2 and Figure 4-2. In general, the *M. nasuta* tissue concentrations are lower than the corresponding *N. caecoides* tissue concentrations. As was observed with the *N. caecoides* tissue concentrations, the relationship between tissue concentrations and the organic carbon-normalized sediment concentrations is stronger than the relationship between the tissue concentrations and the porewater concentrations.

Table 4-2. TBT concentrations in *M. nasuta*, sediment, and porewater

	M. nasuta (µg/kg)			Sediment (µg/kg)		Porewater (µg/L)	
Rank[a]	Wet Weight	Dry Weight	Station	Bulk	TOC-normalized	Filtered	Unfiltered
1	4.0	24.0	TBT-08	400	12,300	0.21	0.38
2	9.0	52.0	TBT-15	530	39,300	0.13	0.24
3	10.0	59.0	TBT-22	350	37,200	0.09	0.29
4	11.0	57.0	TBT-24	570	44,900	0.14	0.33
5	13.0	70.0	TBT-11	130	17,300	0.07	0.10
6	14.0	97.0	TBT-21	610	49,600	0.38	0.51
7	15.0	83.0	TBT-05	680	37,200	0.16	0.22
8	18.0	85.0	TBT-09	800	39,600	0.21	0.27
9	21.0	179	TBT-02	690	34,700	0.27	0.38
10	25.0	152	TBT-12	830	36,100	0.30	0.48
11	25.0	141	TBT-18	210	18,300	0.06	0.08
12	29.8[b]	195	TBT-19	450	36,900	0.06	0.08
13	43.0	297	TBT-28	670	51,100	0.57	0.69
14	47.4[b]	321	TBT-30	310	24,200	0.76	0.90
15	52.0	361	TBT-07	820	48,700	0.16	0.21
16	94.0	528	TBT-14	1,050	93,300	0.45	0.71
17	99.0	627	TBT-04	330	30,000	0.15	0.29
18	177[b]	911	TBT-13	1,100	84,000	0.37	0.47
19	195	1,190	TBT-26	1,100	90,900	0.13	0.17
20	376	2,280	TBT-20	3,500	219,000	0.41	1.01

[a] Rank order determined by TBT concentration in *M. nasuta* (wet weight).
[b] Average of 5 replicate bioassays.

Figure 4-2

4.1 COMPARISON WITH TRIGGER VALUES

None of the measured tissue concentrations exceeded the USEPA Superfund site-specific tissue trigger value of 0.6 μg/g wet weight (3.0 μg/g dry weight) (ESI 1999b). The highest measured tissue concentrations were 0.376 μg/g wet weight for *M. nasuta* and 0.384 μg/g wet weight for *N. caecoides*, both measured in the test conducted with sediment from Station TBT-20.

The measured tissue concentrations of TBT for both *N. caecoides* and *M. nasuta* were low, despite the presence of TBT in both the bulk sediment and porewaters. The relationship between the measured tissue concentrations and the sediment and porewater concentrations of TBT is explored in detail in Section 4.3.

4.2 DELINEATION OF WSOU

The results of the bioaccumulation testing did not identify any of the areas tested as being of concern due to the bioaccumulation of TBT from the sediments.

4.3 COMPARISON OF TISSUE, SEDIMENT, AND POREWATER TBT CONCENTRATIONS

Sediment bioaccumulation testing was conducted using *M. nasuta* and *N. caecoides*, as described in Section 2.2.3. In the following sections, the measured TBT concentrations in tissue for these species are compared with the measured concentrations of TBT in bulk sediment, organic carbon-normalized sediments, and porewater.

For each comparison, exploratory data analyses were used to determine whether there was any evidence of a linear relationship in the original or log-transformed units. Linear regressions were applied to those pairs of variables which had evidence of a linear relationship on some scale. Standard residual diagnostic techniques were used to determine whether the fit of the linear model could be improved by transformation. All statistical analyses were conducted using S-PLUS™ statistical software (Version 4.0, MathSoft, Inc.).

Correlation and regression analyses can be very sensitive to the data distribution, and to outliers (recorded measurements far from the trend of the bulk of the data). For this reason, the data were transformed or outliers were removed in order to assess the impact of outliers on the linear relationship. These actions were intended to result in the most accurate measure of linear association between the two variables, and did not always result in the highest correlation or R^2 value. The parameter estimates displayed in the figures and tables represent the best linear fit for each hypothesized relationship.

It is important to note that R^2 is a descriptive measure of the linear association between the dependent and independent variables in each model. Intercept and slope estimates are given for completeness. The presentation of these estimates does not imply that adequate or meaningful predictions can be made on exact bioaccumulation values using this model. Unbiased calculation of parameter estimates and confidence intervals relies on the assumption that the measurements of the independent variable are obtained without error, or at least that the measurement error is small when compared to the measurement error on the dependent variable (bioaccumulation). For most of these regressions, the independent variable was subject to random measurement error which may or may not be smaller in magnitude than the measurement error in the dependent variable. Hypothesis tests and confidence intervals were intentionally not calculated, since the intercept and slope estimates are likely to be biased.

4.3.1 Comparison of Tissue Concentrations and Sediment Concentrations

A comparison was made between TBT concentrations in tissue and those in bulk sediment (Figure 4-3). A stronger relationship was observed between TBT concentrations in sediment and the tissue concentrations for *N. caecoides* than for *M. nasuta*, which is reflected in R^2 values for each of the regressions (Table 4-3). In addition, the relationship between the tissue concentrations and the organic carbon-normalized sediment TBT concentrations was examined (Figure 4-4). For the complete dataset, the relationship between the tissue concentrations and the organic carbon-normalized sediment concentrations was stronger for both *M. nasuta* and *N caecoides* than the relationship between the tissue concentrations and the bulk sediment concentrations (Table 4-3). When potential outliers are removed, the R^2 values are similar (Table 4-3).

Table 4-3. Relationship between tissue concentrations and bulk and organic carbon-normalized sediment concentrations

Independent variable	Log Transformed?	Dependent variable	Log Transformed?	R^2	Potential outliers	R^2 with outliers excluded
Sediment concentration	Yes	*M. nasuta* tissue conc.	Yes	0.34		
Sediment concentration	Yes	*N. caecoides* tissue conc.	Yes	0.53	TBT-08, TBT-11	0.78

Sediment TOC-normalized	Yes	*M. nasuta* tissue conc.	Yes	0.48		
Sediment TOC-normalized	Yes	*N. caecoides* tissue conc.	Yes	0.75	TBT-08	0.74

Figure 4-3

Figure 4-4

4.3.2 Comparison of Tissue Concentrations and Porewater Concentrations

An initial comparison of TBT concentrations in tissue with TBT concentrations in unfiltered and filtered porewater revealed no relationship between the concentrations in tissue and the concentrations in porewater measured by either method (Figure 4-5).

Concentrations in tissue were then compared to concentrations in porewater normalized for their organic content. TBT concentrations in tissue measured in both species were compared to TBT concentrations measured in unfiltered porewater and normalized to the DOC content of the porewater samples (Figure 4-6). The linear regressions between the tissue concentrations and the porewater concentrations are weak for both species. The equations for the regression lines and the R^2 values are presented in Table 4-4.

Table 4-4. Relationship between tissue TBT concentrations and porewater TBT concentrations

INDEPENDENT VARIABLE	DEPENDENT VARIABLE	R^2	POTENTIAL OUTLIERS	R^2 WITH OUTLIERS EXCLUDED
Unfiltered conc./DOC	*M. nasuta* tissue	0.30		
Unfiltered conc. /DOC	*N. caecoides* tissue	0.23	TBT-20, TBT-26	0.35
Filtered conc./DOC	*M. nasuta* tissue	0.31		
Filtered conc/DOC	*N. caecoides* tissue	0.21	TBT-20, TBT-26	0.55
Dissolved conc.	*M. nasuta* tissue	0.48		
Dissolved conc.	*N. caecoides* tissue	0.75	TBT-08	0.74

TBT concentrations measured in filtered porewater and normalized to the DOC concentrations measured in the porewater samples are compared to TBT concentrations in tissue in Figure 4-7. The relationship between the normalized TBT concentrations in filtered porewater and the concentrations in tissue are similar to those seen between normalized TBT concentrations in unfiltered porewater and the concentrations in tissue. The R^2 values presented in Table 4-3 reflect the variability of the data.

Figure 4-5

Figure 4-6

Figure 4-7

4.4 SEDIMENT-POREWATER RELATIONSHIP

The sediment and the corresponding unfiltered and filtered porewater TBT concentrations are compared in Figure 4-8. The correlations between sediment and both the filtered and unfiltered porewater TBT concentrations were weak (Figure 4-8, Table 4-5). Station 17 was identified as a potential outlier in both plots. Station 10 was identified as a potential outlier in the plot of sediment vs. unfiltered porewater concentrations.

Table 4-5. Relationship between bulk sediment concentrations of TBT and those in filtered and unfiltered porewater

INDEPENDENT VARIABLE	LOG TRANSFORMED?	DEPENDENT VARIABLE	LOG TRANSFORMED?	R^2	POTENTIAL OUTLIERS	R^2 WITH OUTLIERS EXCLUDED
Sediment concentration	Yes	Filtered porewater	Yes	0.56	TBT-17	0.64
Sediment concentration	Yes	Unfiltered porewater	Yes	0.52	TBT-10, TBT-17	0.44

Distribution coefficients (K_d) can be calculated to express the relationship between measured sediment and porewater concentrations.

$$K_d = \frac{C_{sed}}{C_{pw}}$$

where:

C_{sed} = sediment concentration

C_{pw} = porewater concentration

For organic contaminants, organic carbon-normalized distribution or partition coefficients (K_{oc}) are calculated using the following equation:

$$K_{oc} = \frac{K_d}{f_{oc}}$$

where:

f_{oc} = sediment fraction organic carbon

The calculation of K_{oc} values is based on the assumption that the sediment organic carbon is controlling the distribution of the contaminant between the sediment and porewater.

Figure 4-8

The mechanisms controlling the distribution of TBT in sediments are not well understood. In addition to the sediment fraction organic carbon, the chemical characteristics of the sedimentary organic matter, sediment mineralogy, and other sediment properties may influence the sorption behavior of TBT (Unger et al. 1996). Therefore, more variability may be expected in the calculation and use of K_{oc} values for TBT relative to nonpolar organic compounds such as polychlorinated biphenyls.

Two K_{oc} values were calculated for each sediment sample, using the TBT concentrations in unfiltered and filtered porewater. The calculated distribution coefficients ranged over two orders of magnitude. The log K_{oc} values calculated using the unfiltered porewater concentrations ranged from 4.43-6.51. A similar range of values was calculated using the filtered porewater concentrations (log K_{oc}: 4.5-6.51).

The relationship between the measured log K_{oc} values and the measured DOC concentrations in the filtered porewater samples is illustrated in Figure 4-9. There is a trend of decreasing log K_{oc} values with increasing DOC. However, the relationship between the two variables is weak ($R^2 = 0.28$). Therefore, the presence of DOC does not appear to be contributing to the variability seen in the measured log K_{oc} values.

4.5 SUMMARY AND CONCLUSIONS

Bioaccumulation testing was conducted with two species, *N. caecoides* and *M. nasuta*. None of the measured concentrations of TBT in tissue exceeded the USEPA Superfund site-specific tissue trigger value of 0.6 μg/g wet weight (3 μg/g dry weight) or the Respondents' trigger value of 1.0 μg/g wet weight (5 μg/g dry weight) (ESI 1999b). Therefore, none of the areas sampled were identified as areas of concern on the basis of TBT bioaccumulation testing.

Further investigation into the relationships between the measured tissue concentrations and sediment and porewater TBT concentrations revealed that the strongest relationships were observed between tissue concentrations and bulk sediment and organic carbon-normalized sediment concentrations. The relationships between the tissue concentrations and the porewater concentrations were weak. In addition, a strong relationship was not observed between measured sediment and porewater TBT concentrations.

The effect of filtering the porewater samples can be evaluated by comparing the filtered and unfiltered porewater samples. Both the TBT and DOC concentrations were generally lower in the filtered porewater samples relative to the unfiltered samples. The greatest loss of TBT was 69 percent of the unfiltered concentration. The mean change in

Figure 4-9

concentration for all porewater samples was a loss of 30 percent of the unfiltered concentration. The greatest loss of DOC was a loss of 42 percent of the unfiltered DOC concentration. The mean difference for all porewaters was a loss of 7 percent of the unfiltered DOC concentration. There was no consistent relationship between the loss of TBT and the loss of DOC as a result of filtering. It is important to note that all the porewater samples were subject to ultrafiltration. Therefore, the unfiltered porewater DOC concentrations are not representative of the DOC concentrations that would be expected in the undisturbed porewater samples

A complete discussion of the uncertainties associated with the study design, study execution, and data analysis is contained in a separate technical memorandum (ESI 1999b).

5.0
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